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Preparation and Certification of the Isotopic Reference Material IRMM-049d

R. Jakopič, R. Eykens, F. Kehoe,
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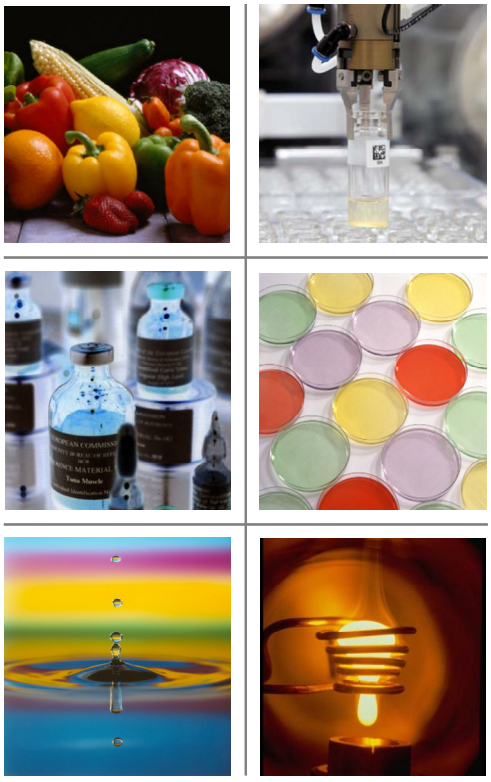

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Summary

A highly enriched ^{242}Pu Isotopic Reference Material (IRMM-049d) has been prepared and certified for the ^{242}Pu isotope amount content. The certified value of 3.666 8(18) $\cdot 10^{-7}$ mol ^{242}Pu per g of solution was established by Isotope Dilution Mass Spectrometry (IDMS). The plutonium isotopic composition was determined by Thermal Ionization Mass Spectrometry (TIMS) and calibration of these measurements by means of synthetic mixtures.

The IRMM-049d Isotopic Reference Material is supplied in a glass ampoule with a screw cap seals containing about 10 mL of 5 mol·L^{-1} nitric acid with plutonium. The content of each ampoule is approximately 1 mg ^{242}Pu.

This Isotopic Reference Material is the product of a systematic IRMM programme to supply Isotopic Reference Materials of various isotopes at different concentrations.

Introduction

IRMM produces and provides solutions of enriched uranium and plutonium isotopes designed for mass-spectrometric isotope dilution measurements of nuclear materials. For the measurement of plutonium, the isotope ^{242}Pu is valuable as a spike because this isotope is usually found only as a minor component in plutonium of the nuclear fuel cycle.

The original certified spike of this isotope was approaching exhaustion and therefore it was decided to replace it by preparing a new stock of the source material and certifying the isotope amount content by IDMS using a ^{239}Pu spike. A concentration of *ca.* 0.1 mg/g solution was chosen and deemed to be convenient for many types of measurements of plutonium.

Preparation of the ^{242}Pu Isotopic Reference Material

Preparation of a stock ^{242}Pu solution

A ^{242}Pu stock solution was prepared by dissolving plutonium metal (BC 975B) of a French (CETAMA) origin in 5 mol·L^{-1} HNO_3 (p.a., Merck, Darmstadt). This stock solution containing about 614 mg ^{242}Pu was purified as described in the following.

Purification of a stock ^{242}Pu solution

The plutonium solution was evaporated to dryness and dissolved in 24 mL 2 mol·L^{-1} HNO_3. To achieve valency homogenisation in the Pu^{+4} state, 4 mL 1.25 mol·L^{-1} $FeCl_2$ was added to convert all Pu to Pu^{+3} valency state. Subsequently, 12 mL 1 mol·L^{-1} $NH_2OH{\cdot}HCl$ and 12 mL 1 mol·L^{-1} $NaNO_2$ were added. Finally, 52 mL concentrated nitric acid (65%, Merck, Darmstadt) was added to obtain a Pu^{+4} 8 mol·L^{-1} HNO_3 solution.

Two glass columns with a diameter of 2.5 cm and a height of 15 cm were used in parallel and were filled with Bio-Rad AG1-X4 (100-200 mesh) resin in chloride form for the purification. The plutonium solution was transferred onto the columns. After both columns were washed with 350 mL 8 mol·L^{-1} HNO_3, Pu was eluted from the column with 1 L of 0.35 mol·L^{-1} HNO_3.

Dilution and ampouling of ^{242}Pu solution

The eluted Pu fractions were combined, evaporated to dryness and dissolved in 61.44 g 5 mol·L^{-1} HNO_3 to obtain a 10 mg Pu per g solution. From that purified Pu solution, a 10.46 g fraction was taken into a flask and diluted to 1007.1 g with 5 mol·L^{-1} HNO_3 to obtain the final concentration of the ^{242}Pu of 0.1 mg Pu per g solution. This solution was dispensed into 93 screw-cap glass ampoules providing *ca*. 10 mL per ampoule.

Plutonium isotopic composition of IRMM-049d

The isotopic composition of plutonium was established by measuring isotope abundance ratios on an ampoule of the IRMM-049d on a Triton TIMS (Thermo Fisher Scientific Inc., USA).

Prior to mass spectrometry measurements a chemical separation was performed to obtain a purified Pu solution (*RM WI/0352: Separation and purification of plutonium samples for measurements of isotopic ratios by TIMS)*. The purified fraction of Pu was prepared in 1 $mol \cdot L^{-1}$ HNO_3. About 50 ng of Pu solution was put on an evaporation filament using a transfer pipette and dried by passing an electrical current through the filament.

A magazine was loaded with six filaments of IRMM-049d and nine filaments of IRMM-290/A3 plutonium isotopic reference material for the calibration of the mass spectrometer for mass fractionation. The isotopic composition of the samples was measured using the total evaporation technique on a Triton TIMS (*RM WI/0360: Measurement of Plutonium isotopic ratios by TIMS_TRITON).* The measurement was continued until the sample has been exhausted. This is done in order to minimize mass fractionation effects.

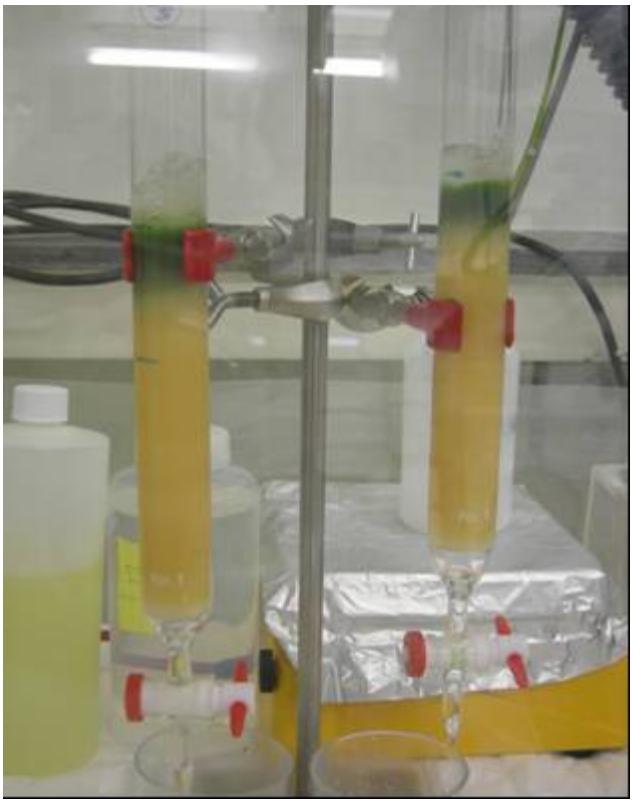

Figure 1: Purification of Pu stock solution by anion exchange.

The observed Pu isotope ratios were corrected for mass fractionation by measuring the IRMM-290/A3 isotopic standard on the same magazine applying the same procedure. The correction factor (K) for mass fractionation was calculated from nine replicate measurements of IRMM-290/A3 and was determined to be $K_{242/239}$ = 0.99983(20). Correction factors for all other Pu isotope ratios were derived from $K_{242/239}$ and were in the range of 0.99972 - 1.0001 with a relative standard uncertainty of 0.0033-0.017 %.

The certified values for the plutonium isotope ratios are listed in Table 1 and are valid for 1 July 2010. The expanded uncertainties were estimated according to the ISO Guide to the Expression of Uncertainty in Measurement (GUM). They apply to the last two digits of the value.

The main components to the final uncertainty are the IRMM-290/A3 plutonium isotopic standard and the K-factor for the respective isotope ratio.

Table 1: Isotope amount ratios and isotopic composition of plutonium in IRMM-049d valid for 1 July 2010. Expanded uncertainties are given in brackets (coverage factor k=2).

Certified amount ratios	
$n(^{238}Pu)/n(^{242}Pu)$	0.005 341 8(69)
$n(^{239}Pu)/n(^{242}Pu)$	0.002 221 6(13)
$n(^{240}Pu)/n(^{242}Pu)$	0.046 070(35)
$n(^{241}Pu)/n(^{242}Pu)$	0.002 990 4(21)
$n(^{244}Pu)/n(^{242}Pu)$	0.000257 13(84)

Amount fraction (·100)		Mass fraction (·100)	
$n(^{238}Pu)/n(Pu)$	0.505 44(64)	$m(^{238}Pu)/m(Pu)$	0.497 30(63)
$n(^{239}Pu)/n(Pu)$	0.210 21(12)	$m(^{239}Pu)/m(Pu)$	0.207 69(12)
$n(^{240}Pu)/n(Pu)$	4.359 0(31)	$m(^{240}Pu)/m(Pu)$	4.325 0(31)
$n(^{241}Pu)/n(Pu)$	0.282 94(19)	$m(^{241}Pu)/m(Pu)$	0.281 91(19)
$n(^{242}Pu)/n(Pu)$	94.618 1(36)	$m(^{242}Pu)/m(Pu)$	94.663 6(36)
$n(^{244}Pu)/n(Pu)$	0.024 329(79)	$m(^{244}Pu)/m(Pu)$	0.024 543(80)
The molar mass of the plutonium in this sample is 241.942 417(79) $g \cdot mol^{-1}$			

Certification of ^{242}Pu amount content of IRMM-049d

The certification of the plutonium amount content of Isotopic Reference Material IRMM-049d was achieved by IDMS. Six ampoules of IRMM-049d were randomly selected from the batch. The plutonium solution in IRMM-049d was split over two vials of IRMM-1027m (^{239}Pu) for IDMS analysis. IRMM-1027m is a large-sized dried spike in which approximately 2 mg Pu and 50 mg U, enriched to 20 % ^{235}U, per g solution are dried into individual vials. The enriched ^{239}Pu in this spike has been certified from the mass of pure plutonium metal and verified by IDMS [1]. The spike is primarily designed for measurement of U and Pu amount contents in solutions of spent nuclear fuel but the certification of the ^{239}Pu amount content renders it highly suitable for the IDMS measurement of IRMM-049d. Furthermore by using IRMM-1027m the certification of IRMM-049d becomes part of the ongoing compatibility study inter-linking selected IRMM plutonium spikes on a metrological basis applying state-of-the art measurement procedures [2]. In total 12 blend mixtures were prepared.

The series of 12 blend mixtures described above were used to assess the homogeneity of the plutonium and to certify the amount content of ^{242}Pu in IRMM-049d. The blend mixtures were heated to dryness and then chemically conditioned. Pu fractions were separated by the standard anion exchange method (*RM WI/0354: Separation and purification of uranium and plutonium mixtures for measurements of isotopic ratios by TIMS)*. The excess of uranium in the mixed U/Pu spike IRMM-1027m means that extra separation steps were needed before the measurement of

the Pu isotope ratios. Three consecutive separations for each blend mixture were performed in order to obtain a purified Pu fraction and to avoid interferences with uranium coming from IRMM-1027m in mass spectrometric measurements. Three magazines were loaded with four filaments for each blend; the remaining positions were filled by IRMM-290/A3 standards. The plutonium isotope ratios $n(^{239}Pu)/n(^{242}Pu)$ were measured on the Triton TIMS [3] applying a total evaporation technique. The results of these IDMS measurements for the ^{242}Pu amount content are given in Figure 2.

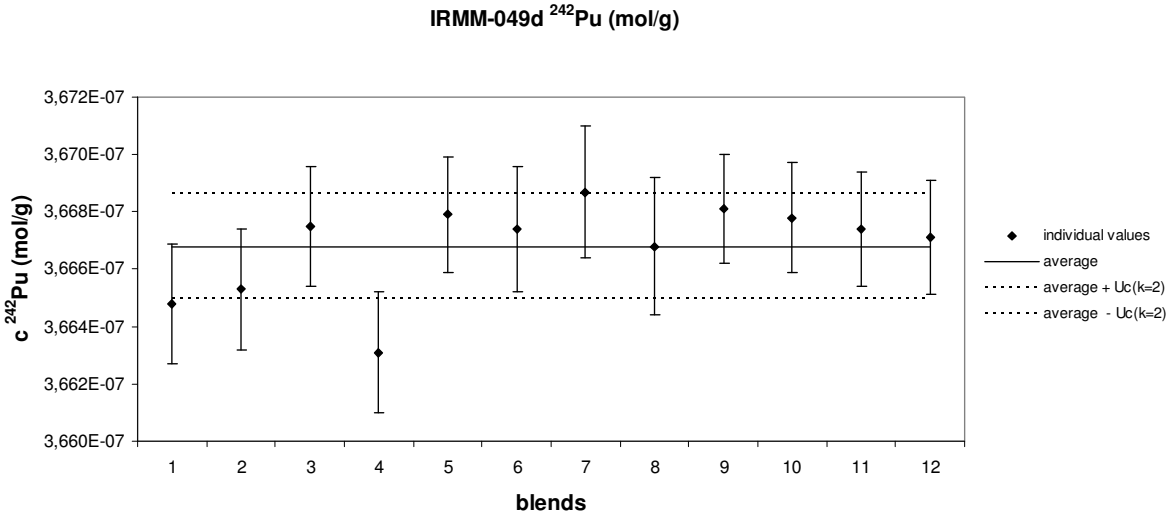

Figure 2: The amount content of ^{242}Pu in blends of IRMM-049d measured by IDMS (with expanded uncertainties, coverage factor k=2).

Using the ^{239}Pu spike (IRMM-1027m), the ^{242}Pu amount content in IRMM-049d can be determined by IDMS through a measurement of the isotope ratio $R(b) = n(^{239}Pu)/n(^{242}Pu)$ in a blend via the following equation:

$$c\left(^{242}Pu, x\right) = c\left(^{239}Pu, y\right) \cdot \frac{m(y)}{m(x)} \cdot \frac{R(y) - R(b)}{R(b) - R(x)} \cdot \frac{1}{R(y)}, \text{ where}$$

$c(^{242}Pu, x)$: amount content of ^{242}Pu in the IRMM-049d
$c(^{239}Pu, y)$: amount content of ^{239}Pu in the spike
m(x): mass of the IRMM-049d
m(y): mass of the spike
$R(b)$: isotope amount ratio $n(^{239}Pu)/n(^{242}Pu)$ of the blend
$R(x)$: isotope amount ratio $n(^{239}Pu)/n(^{242}Pu)$ of the unspiked IRMM-049d
$R(y)$: isotope amount ratio $n(^{239}Pu)/n(^{242}Pu)$ of the spike

The certified value for the ^{242}Pu amount content was calculated as the mean value of twelve certification measurement results and is 3.666 8(18) $\cdot 10^{-7}$ mol·g^{-1}. The expanded uncertainty with a coverage factor $k=2$ is given in parentheses and corresponds to a level of confidence of about 95 % estimated according to the ISO Guide to the Expression of Uncertainty in Measurement (GUM). It applies to the last two digits of the value. The major component to the expanded uncertainty comes from the spike isotopic reference material IRMM-1027m. Figure 3 shows the relative contribution of the main uncertainty components to the overall uncertainty of the certified value in IRMM-049d.

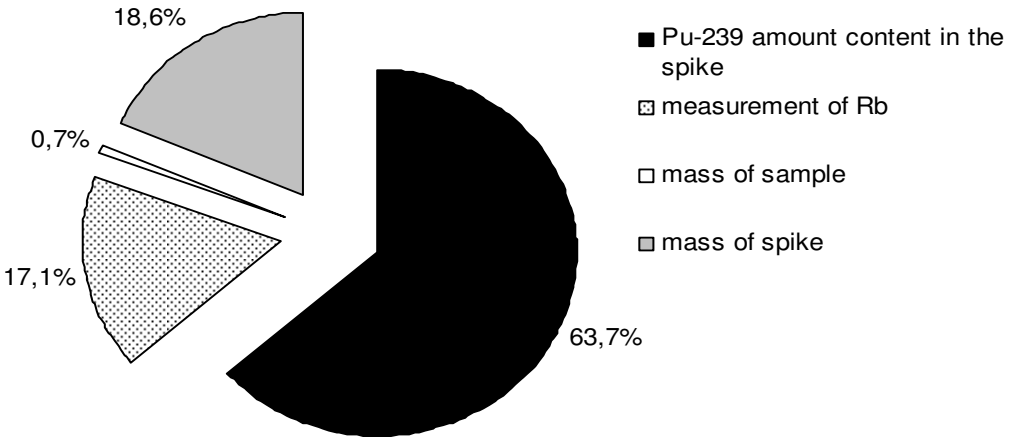

Figure 3: The uncertainty budget of the major components for ^{242}Pu amount content in IRMM-049d.

The value of the plutonium isotopic amount content in IRMM-049d is traceable to the SI via the certified IRMM-1027m spike reference material in combination with identification and quantification of the sources of uncertainties for IDMS according to the ISO Guide to the Expression of Uncertainty in Measurement (GUM) [4].

Conclusion

A new ^{242}Pu Isotopic Reference Material (IRMM0-49d) has been prepared and certified for its ^{242}Pu amount content. The certified value of 3.666 8(18) $\cdot 10^{-7}$ mol ^{242}Pu per g of solution was established by Isotope Dilution Mass Spectrometry (IDMS) and is metrologically traceable to the SI. IRMM-049d extends the inter-calibration campaign using state-of-the art measurement procedures to underpin the confidence in the use of IRMM isotopic plutonium reference materials for nuclear material and environmental sample measurements.

Acknowledgment

The authors would like to thank Dr. Roger Wellum for the certification file review.

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